Electronic Supplementary Information for

Deformable nature of various damaged DNA duplexes estimated by an electrochemical analysis on electrodes

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Experimental Section

Materials. DNA probes (Fc1 and Fc2) and CPD or 6–4PP containing oligomers were synthesized according to the procedure previously reported. Fully-matched and ADTHF containing complements were all commercially available.

Preparation of probe-modified gold electrodes. Commercially available gold electrodes (Tanaka Kikinzoku, Tokyo, Japan) were cleaned as a reported procedure and dried under argon stream before use. For immobilization of DNA probes, 1 µL of a probe DNA (100 µM) in a buffer solution (10 mM sodium cacodylate that contained 0.5 M NaCl, pH 7.0) was placed on the gold electrode and kept in a closed container under high humidity for 90 min at room temperature. After having been rinsed with the buffer solution (300 µL), the probe DNA-modified gold electrode was soaked in a solution of 1 mM 6-mercaptohexan-1-ol in the buffer solution contained 1% Tween 20 (300 µL) for 90 min at room temperature. Then, it was thoroughly washed with Milli-Q water and the buffer solution successively. For hybridization of target DNAs, 5 µL of a target DNA (10 µM) in the buffer solution was placed on the probe-modified gold electrode and kept in a closed container under high humidity for 90 min at room temperature, then it was rinsed with the buffer solution (300 µL).

Electrochemical measurements. CV measurements were carried out in a buffer solution (10 mM sodium cacodylate that contained 0.5 M NaCl, pH 7.0) at 15 °C on the probe-modified electrodes by means of a normal three-electrode configuration consisting of the gold working electrode, a saturated Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The working compartment of the electrochemical cell was separated from the reference compartment by a glass frit.

MALDI-TOF Mass Measurements. MALDI-TOF mass spectra were recorded on a Bruker-Daltonics-Autoflex mass spectrometer operating in the negative ion mode with 3-hydroxypicolinic acid as a matrix. Fc1: calcd for [M–H], C162H195FeN57O88P15S: 4900.77; found 4900.46, Fc2: calcd for [M–H], C179H215FeN67O99P17S: 5502.85; found 5500.41.
**T_{m} Measurements.**  
*T_{m}* melting curves (1.0 °C/1.0 min) were obtained by JASCO V-560 UV/VIS spectrophotometer with a peltier and a temperature controller in a temperature range from 20 to 90 °C (10 mm pathlength). The *T_{m}* values were determined from the maxima of the first derivatives of the melting curves measured in a buffer solution: 10 mM sodium cacodylate (pH 7.0), 0.5 M NaCl. Errors were estimated at ± 1.0 °C.

**References for ESI**

S1  

S2  
Figure S1. Typical CD spectra at 25 °C of ds-DNAs for (A) native 1•Wild$_{14}$ and (B) photo-damaged 1•6–4PP$_{14}$. CD spectra were recorded on a JASCO-J-720WI spectropolarimeter. Each CD spectrum of 1 (1 µM) with 1 equiv of Wild$_{14}$ or 6–4PP$_{14}$ (1 µM) was measured in 10 mM sodium cacodylate that contained 0.5 M NaCl (pH = 7.0).
Figure S2. Scan rate $v$ dependence of the anodic peak current $i_{pa}$ ($i_{pa}/v^{1/2}$ vs log($v$)) of the cyclic voltammograms recorded at the Fc1-modified gold electrodes with (A) Wild$_{14}$, (B) CPD$_{14}$, (C) AP$_{14}$, (D) a single-base mismatched complement AT$_{14}$, (E) 6–4PP$_{14}$, and (F) a two-base mismatched complement AA$_{14}$. 
Figure S3. Scan rate $v$ dependence of the anodic peak potential $E_{pa}$ ($\Delta E_{pa}$ vs log($v$)) of the cyclic voltammograms recorded at the Fe1-modified gold electrodes with (A) AP$_{14}$, (B) CPD$_{14}$, and (C) 6–4PP$_{14}$. 

$k = 202$ s$^{-1}$

$k = 98$ s$^{-1}$

$k = 240$ s$^{-1}$